

## Component Selection, Accelerated Testing, and Improved Modeling of AMTEC Systems for Space Power

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Alkali metal thermal to electric converter (AMTEC) designs for space power are numerous, but selection of materials for construction of long-lived AMTEC devices has been limited to electrodes, current collectors, and the solid electrolyte. AMTEC devices with lifetimes greater than 5 years require careful selection and life testing of all hot-side components. The likely selection of a remote condensed design for initial flight test and probable use with a radioisotope heat source in AMTEC powered planet probes requires the device to be constructed to tolerate operating  $T > 1150\text{K}$ , as well as exposure to  $\text{Na}_{(g)}$ , and  $\text{Na}_{(liq)}$  on the high pressure side. The temperatures involved make the characterization of high strength and chemical resistance to Na containing  $\text{Na}_2\text{O}$  critical. Selection among materials which can be worked should not be driven by ease of fabricability, as high temperature stability is the critical issue. These concepts drive the selection of Mo alloys for  $\text{Na}_{(liq)}$  containment in AMTEC cells for  $T$  to  $1150\text{K}$  operation, as they are significantly stronger than comparable Nb or Ta alloys, are less soluble in  $\text{Na}_{(liq)}$  containing dissolved  $\text{Na}_2\text{O}$ , are workable compared with W alloys (which might be used for certain components), and are ductile at the  $T > 500\text{K}$  of proposed AMTEC modules in space applications. Either a wick with  $\mu\text{m}$ -scale pores, or an electromagnetic pump at  $T < 500\text{K}$ , with a throat dimension of about  $0.1\text{ mm}$  to recirculate the Na working fluid, require that the volatility of structural alloys used with high temperature  $\text{Na}_{(liq)}$  must be far less than would lead to containment failure; precipitation of dissolved metal in the high temperature end of the wick or transport of dissolved metal down a temperature gradient to the electromagnetic pump, could lead to failure. AMTEC components should be tested using the same procedures of testing employed with electrode life testing: evaluation of aging phenomena via microscopic analysis at times well before failure or

even macroscopically detectable change, fundamental modeling using physical parameters and minimal empiricism, and verification of accelerated test procedures with comparison to normal life tests. Some compromises of system design to accommodate materials life issues may also be required. For example, a favorable design includes hot feedthroughs to series/parallel connection of the individual AMTEC modules. Feedthrough temperature may be constrained by the attack of sodium vapor on hot  $\alpha\text{-Al}_2\text{O}_3$  at high temperature; however, a feedthrough slightly cooler than the hot side temperature may introduce negligible thermal losses and greatly increase life. These sorts of compromises lead to model complexity. Evaluation of laboratory cell performance has already invalidated the assumptions of early systems studies. For example, high current rates and hence high sodium gas flow to the condenser was found to reduce radiative losses in a 13% efficient cell compared with lower current rates where thermal losses were greater because an ideal reflective Na film had not formed on all surfaces. These complications hinder unverified extrapolation from simple models, but experimental evaluation of phenomena observed in AMTEC cells allows the development of more realistic, if somewhat complex models. This paper will provide an assessment of some of the materials and components required for high performance AMTEC devices for space applications.

Basic models for AMTEC cell operation include a fundamental electrode performance model and an electrode life model which have been compared to experimental performance results. [Weber, 1974; Williams, *et al.*, 1990a,b] Recent work indicates that several AMTEC electrode have the potential for the potential for high performance and long life. [Williams, *et al.*, 1989; Ryan, *et al.*, 1991, 1992, 1993] Other AMTEC components still present problems,

although some issues have little experimental or fundamental basis. The status of these problems will be discussed in this paper, with the goal of focusing attention on critical problems, and correcting some mis-impressions about other issues. Systems-design issues will not be discussed in detail here. Fluid management issues, including recirculation and zero-g fluid management are critical and are addressed by several other papers in this symposium.

AMTEC issues which have been identified in the past several years include the following:

1. Component volatility and migration in the context of operating temperatures of cell
2. Containment strength at temperature
3. Containment corrosion by sodium
4. Electrolyte stress and stability
5. Electrolyte/metal braze seal

### 1. Component volatility and migration and operating temperatures of cell

Vapor pressures of most elements and many compounds stable at high temperature are readily available in compilations, or may be readily calculated from thermochemical data, [Alcock, *et al.*, 1984] Recently, the possibility of operating sodium fluid AMTECs efficiently at temperatures as low as 873K, utilizing the low electrode losses of oxidized Mo electrodes has been proposed. Neither high efficiency nor high power densities have yet been verified experimentally, but the low transport and electrode kinetics losses of Mo electrodes containing sodium molybdate,  $\text{Na}_2\text{MoO}_4$ , and the ionic conductivity of  $\text{Na}_2\text{MoO}_4$  have been determined experimentally. [Williams, *et al.*, 1986a,b; Williams, *et al.*, 1988] The phase diagram of stable Na-Mo-O phases at sodium activities of interest for AMTEC has also been determined, and indicates that  $\text{Na}_2\text{MoO}_4$  is the stable phase at moderate sodium activities, but converts to  $\text{Na}_2\text{Mo}_3\text{O}_6$  by oxidizing Mo at low sodium activities characteristic of AMTEC open circuit conditions. Enthalpies of  $\text{Na}_2\text{MoO}_4$ 's phase transitions have been measured, as has the vapor pressure of liquid  $\text{Na}_2\text{MoO}_4$ . [Denielou, *et al.*, 1971; Ermilova, *et al.*, 1976] These data allow the vapor pressures of the solid phases to be calculated,

and the composite vapor pressure curve is shown in Fig. 1. The stability and volatility of sodium molybdate is also relevant to corrosion processes of liquid sodium on Mo alloy containers, since  $\text{Na}_2\text{O}$  present in small concentrations will be rapidly removed to low temperature zones of the device, where ideally it can be deposited safely.

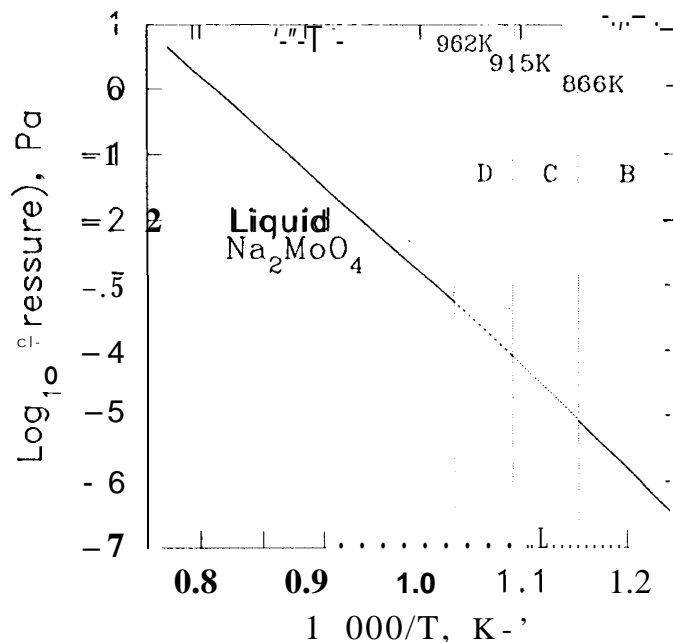


Fig. 1. Vapor pressure of  $\text{Na}_2\text{MoO}_4$  from thermochemical data.

### 2. Containment strength at temperature

A great deal of information is available about the high temperature strength and liquid metal corrosion of refractory alloys. Much of this work was carried out in the 1960's and 1970's and relatively few investigations have been carried out recently. [DiStefano, 1989] In almost all cases, alloys are superior to pure elements for structural purposes at high temperatures in order to minimize grain growth and the consequent decline in strength. Fig. 2. provides a compilation of typical tensile strength data for recrystallized refractory metals and alloys selected from several volumes published by Battelle in 1963. [Schmidt and Ogden, 1963a-d] Recrystallization conditions were not identical, but the temperatures at which alloys lose strength substantially are indicated.

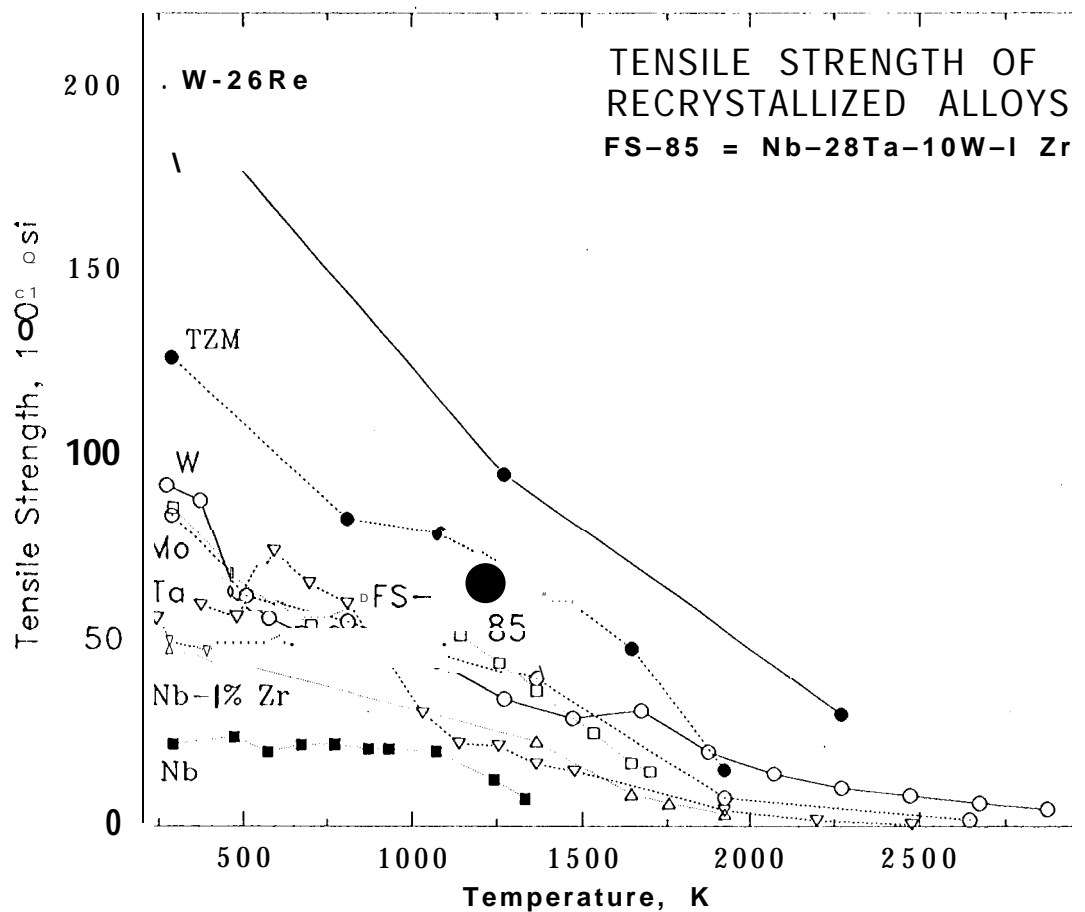


Fig. 2, Typical tensile strengths of refractory metal alloys,

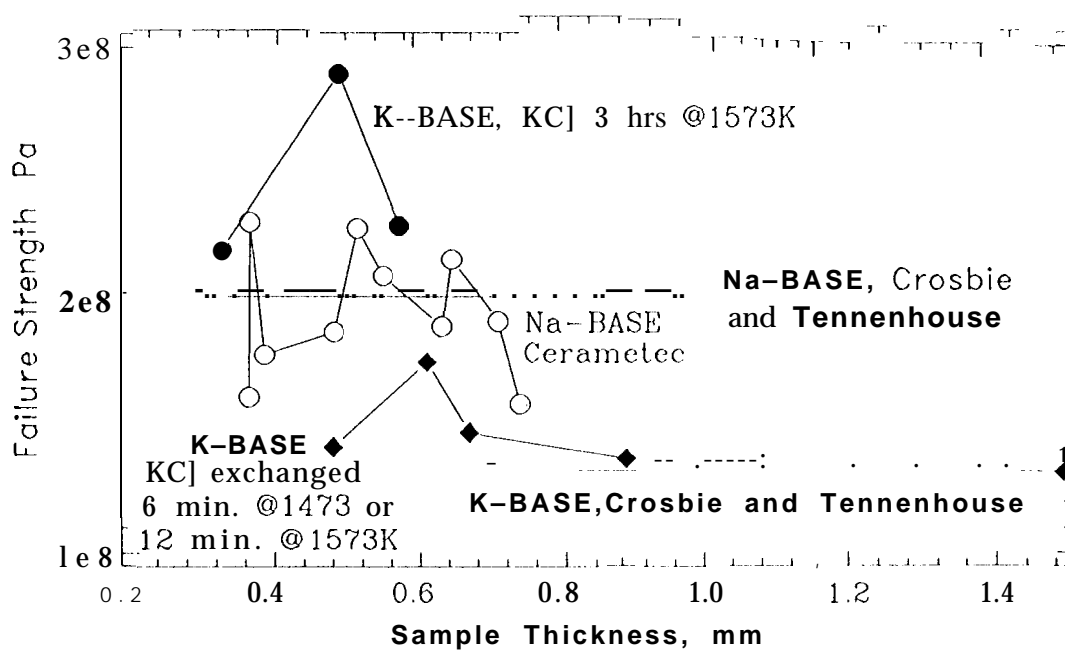


Fig. 3. Increase in Failure Strength of K-BASE by Annealing

### 3. Containment corrosion by sodium

High temperature critical applications of refractory metals for sodium containment have recently indicated the superiority of Mo base alloys, and in particular Mo/Re alloys. Corrosion of both ferrous metal alloys and most refractory metals is substantially accelerated by oxygen dissolved in sodium. [DiStefano, 1989] but low levels of dissolved oxygen are apparently not deleterious to molybdenum and tungsten as the volatility of sodium molybdate and tungstate tend to remove oxygen from high temperature regions. In contrast, dissolution of oxygen in Nb and Ta require either that oxygen levels be kept low by means of getters such as Zr and Hf in the sodium stream, or by alloying with Ti and Zr, in particular. These elements also reduce grain growth and enhance high temperature mechanical strength.

### 4. Electrolyte stress and stability

Relatively little work has been carried out on the kinetic and thermodynamic stability of the  $\beta''$ -alumina phase since the early studies in the 1960's and 1970's, which emphasized the  $\beta$  phase. Two comparative recent papers have dealt with the kinetics of the  $\beta''$  to  $\beta$  transition, which also references early work and a study of the high pressure, high temperature thermodynamic stability of the two phases. [Hedge, 1983; Roth and DeVries, 1977] These papers clarify the stability issue, but do not fully resolve it, as recent results in our laboratory on K  $\beta''$ -alumina suggest that the  $\beta''$  to  $\beta$  transition, studied by Hedge with the Na analog, may have a rate substantially affected by the ambient alkali metal oxide activity. We have taken advantage of this result to synthesize K-BASE at a higher temperature than normally employed, by K<sup>+</sup> ion substitution reactions. Fig. 3 shows the three point strength at failure test results on this ceramic and compares it to our results with commercial Na-BASE and K-BASE exchanged at lower temperatures, and with earlier results. [Crosbie and Tennenhouse, 1982] Tests in our laboratory and in others have revealed that moderate levels of Ca<sup>2+</sup> contamination of sodium can lead an increase in the electrolyte resistance,

although we have not observed mechanical failure as a result. It is clear that many of the issues about the "instability" of BASE at AMTEC operating temperatures are not grounded in experiment or fundamental studies, but assume electrolyte problems which exist in sodium batteries at lower temperatures must also affect AMTEC. This is often not the case: while we found deleterious effects of Ca in Na, small levels of K contamination are apparently unimportant for AMTEC operation, while K<sup>+</sup> segregates at grain boundaries in the BASE at lower temperatures.

### 5. Electrolyte/metal braze seal

The braze seal has been identified as a significant issue for AMTEC, and the commonly used alloy, a Ti/Cu/Ni alloy was of concern due to its low melting point, possible brittleness at room temperature, and possibility of extended attack of Ti on the BASE at operating temperatures. Recent results with a 1850 hour test at JPL have indicated that interdiffusion of niobium into the braze seal, followed by bulk interdiffusion, may alleviate these problem by formation of a Nb/Ti alloy with traces of Ni and Cu.

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### References

- Alcock, C. B.; Itkin, V. P.; Horrigan, M. K.; *Can. Metallurg. Quart.*, 1984, 23, 309
- Crosbie, G.; Tennenhouse, G.; *J. Amer. Ceram. Soc.*, 1982, 65, 187
- Denielou, Lo; Fournier, Y.; Petit, J. P.; Tequi, C.; *C. R. Acad. Sci Paris*, 1971, 272, 1855

DiStefano, J. R.; *J. Mater. Eng.*, **1989**, **11**, **215**

Ermilova, I.O.; Kayenas, E.K.; Zviadadze, Zh. Fiz. Khim., 1976, *SO*, 2172

Ryan, M. A.; Jeffries-Nakamura, B.; Williams, R. M.; Underwood, M. L.; O'Connor, D.; Kikkert, S.; in *Proc. 27th IECEC*; Bland, T., Ed., SAE, Warrendale, PA, 1992, 3, 7.

Ryan, M. A.; Kisor, A.; Williams, R. M.; Jeffries-Nakamura, B.; Underwood, M. L.; O'Connor, D.; in *Proc. 28th IECEC*; (this volume) ACS, 1993

Ryan, M. A.; Jeffries-Nakamura, B.; O'Connor, D.; Underwood, M. L.; Williams, R. M.; *Proc. Sym. on High Temp. Electrode Mat. Char.*, Macdonald, D. D.; Khandkar, A. C.; eds., The Electrochem. Soc., 1991, *Proc. Vol.* 91-6, 115.

Schmidt, F. F.; Ogden, H. R.; *The Engineering Properties of Columbium and Columbium Alloys*, DMIC Rpt. 188, Defense Metals Information Center, Columbus, OH, 1963a

Schmidt, F. F.; Ogden, H. R.; *The Engineering Properties of Tantalum and Tantalum Alloys*, DMIC Rpt. 189, Defense Metals Information Center, Columbus, OH, **1963b**

Schmidt, F. F.; Ogden, H. R.; *The Engineering Properties of Molybdenum and Molybdenum Alloys*, DMIC Rpt. 190, Defense Metals Information Center, Columbus, OH, **1963c**

Schmidt, F. F.; Ogden, H. R.; *The Engineering Properties of Tungsten and Tungsten Alloys*, DMIC Rpt. 191, Defense Metals Information Center, Columbus, OH, **1963d**

Weber, N., *Energy Convers.* 1974, 14, 1

Williams, R. M.; Loveland, M. E.; Jeffries-Nakamura, B.; Underwood, M. L.; Bankston, C. P.; Leduc, H.; Kummer, J. T.; *J. Electrochem. Soc.*, **1990a**, **137**, **1709**,

Williams, R. M.; Jeffries-Nakamura, B.; Underwood, M. L.; Bankston, C. P.; Kummer, J. T.; *J. Electrochem. Soc.*, **1990b**, **137**, **1716**.

Williams, R. M.; Nagasubramanian, G.; Khanna, S. K.; Bankston, C. P.; Thakoor, A. P.; Cole, T.; *J. Electrochem. Soc.*, **1986a**, **133**, **1587**

Williams, R. M.; Bankston, C. P.; Khanna, S. K.; Cole, T.; *J. Electrochem. Soc.*, **1986b**, **133**, **2253**

Williams, R. M.; Wheeler, B. L.; Jeffries-Nakamura, B.; Loveland, M. E.; Bankston, C. P.; Cole, T.; *J. Electrochem. Soc.*, **1988**, **135**, **2738**

Williams, R. M.; Jeffries-Nakamura, B.; Underwood, M. L.; Wheeler, B. L.; Loveland, M. E.; Kikkert, S. J.; Lamb, J. L.; Cole, T.; Kummer, J. T.; Bankston, C. P.; *J. Electrochem. Soc.*, **1989**, **136**, **893**